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SECOND PAPER.

ON PARABROMBENZYL COMPOUNDS.

WOODBURY LOWERY.

Parabrombenzylalcohol($C_6H_4Br\,CH_2\,OH.$)— This substance was most easily prepared by boiling parabrombenzylbromide with water, in a flask with a return-cooler, for two or three days, until it no longer attacked the eyes. The reaction ran as follows: $C_6H_4BrCH_2Br + H_2O = C_6H_4BrCH_2OH + HBr$. The presence of the hydrobromic acid was established by treating the acid aqueous filtrate with argentic oxide, when argentic bromide was formed, and the solution became neutral. This method is analogous to that employed by Grimaux [*] for converting tollylenebromide into tollyleneglycole, except that Grimaux heated the haloid compound with water at 170° to 180°, while I obtained the alcohol by boiling in a flask with a reverse-cooler. The action of water on benzylchloride at high temperatures has been very thoroughly studied: the first research in this field having been undertaken by Limpricht [†] as early as 1866, who by heating the two substances to 190° obtained anthracene, a hydrocarbon $C_{14}H_{14}$, later identified by Van Dorp [‡] as benzyltoluol, and benzylether, which he supposed was formed from benzylalcohol; but neither he, nor Van Dorp, nor Zincke, [§] who afterward made out the theory of this reaction, mentioned obtaining benzylalcohol in this way. The alcohol was also obtained in the ordinary way by heating parabrombenzylacetate with aqueous ammonia in a sealed tube to 160°. The alcohol in whichever way prepared was purified by crystallization from boiling water, and its composition established by the following combustion: —

	Required for $C_7H_6Br.OH$.	Found.
Carbon	44.92	44.94
Hydrogen	3.74	3.99

Properties. — It forms long elastic transparent colorless flattened needles, with a brilliant pearly lustre and a disagreeable odor; its vapor does not attack the eyes. Melting-point, 69°. It burns with a luminous green-bordered flame, distils with steam although slowly, and is very slightly soluble in cold, more freely in boiling water, easily soluble in alcohol, ether, benzole, and carbonic disulphide.

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[*] Grimaux, Comptes Rend., 70, p. 1363; Ann. Chem. Pharm., 155, p. 338.

[†] Limpricht, Ann. Chem. Pharm., 139, 303.

[‡] Van Dorp, ib., 169, 207.

[§] Zincke, Ber. D. Ch. G., 1874, 276.

The *parabrombenzylacetate* ($C_6H_4Br.CH_2\,C_2H_3\,O_2$) was not obtained in a condition pure enough for analysis. On adding water to the alcoholic solution left after boiling parabrombenzylbromide with sodic acetate and absolute alcohol, a more or less dark-colored oil which did not attack the eyes or nose was precipitated: this was dried and fractioned. In the first rectification the greater part came over at about 253°, but on fractioning again a considerable portion came over at lower temperatures; the oftener it was distilled, the less constant became the boiling-point, and after several distillations crystals appeared both in the residue and distillate, while nearly one quarter of the entire amount came over below 100°, and another quarter below 247°; all these fractions attacked the eyes with great energy, whereas the acetate before fractioning did not possess this property; the crystals were little white needles which dissolved readily in ammonic hydrate, and gave a silver salt which was analyzed. 0.2822 gr. of the salt gave 0.1009 gr. of Ag.

	Required for $C_6H_4Br.\,COO\,Ag$.	Found.
Silver	35.06	35.75

As the acid melted at 240° to 250°, there could be no doubt that it was parabrombenzoic acid. Unfortunately the amount of parabrombenzylacetate at my disposal was so small that it was impossible to isolate the other products of this interesting decomposition, and the complete study of this reaction must therefore be postponed until next year, when it will be undertaken in this laboratory.

The acetate before fractioning was an oily liquid heavier than water, having an agreeable odor distantly resembling that of acetic ether, and burning with a luminous green-bordered flame; the boiling-point could not be determined with accuracy on account of the decomposition described above, but probably lies between 250° and 260°.

Parabrombenzylcyanide ($C_6H_4Br.\,CH_2\,CN$), was obtained by boiling parabrombenzylbromide with an alcoholic solution of potassic cyanide as long as potassic bromide was formed; on addition of water a yellow oil was precipitated, which deposited crystals after standing for some time, and finally solidified completely. The crystals were drained on filter-paper, and purified by crystallization from alcohol. Their composition was determined by the following volumetric nitrogen determination: —

0.3565 gr. substance gave 20 cc. nitrogen under a pressure of 742 mm., and a temperature of 9°.

	Required for $C_7H_6Br.CN$.	Found.
Nitrogen	7.10	6.58

Properties. — The substance separates from the oil at first obtained, either in flat truncated octahedra with a marked basal cleavage belonging either to the tetragonal or orthorhombic system, and having a very strong resemblance to the crystals of ferrocyanide of potassium, or else in flat twins imitating in a very beautiful manner the architectural forms of the trefoil and quatrefoil. These crystals are yellowish white, but the substance is rendered colorless by crystallization from alcohol; it has a disagreeable odor, does not attack the eyes, melts at 46°, burns with a luminous green-bordered flame, and is insoluble in water, moderately soluble in cold, freely in hot alcohol, soluble in ether and glacial acetic acid, still more readily in carbonic disulphide and benzole; by boiling with alcoholic potassic hydrate or heating in a sealed tube with hydrochloric acid it is easily converted into parabromalphatoluylic acid. It is to be remarked that the chlorbenzylchloride, according to the observations of Neuhof,* gave when heated as above with alcoholic potassic cyanide, the amide of chloralphatoluylic acid, the cyanide being obtained only by heating the substances in a sealed tube; this difference in the behavior under like conditions of two substances so nearly related as chlorbenzylchloride and parabrombenzylbromide is interesting.

Parabromalphatoluylic Acid ($C_6H_4Br.CH_2COOH$). This substance was most easily obtained by heating the cyanide with crude fuming hydrochloric acid to 100° in a sealed tube. On cooling, the liquid was found to be full of shining flattened needles of the acid, another portion of which had fused on the side of the tube; this method gave better results more neatly than the saponification with potassic hydrate; the acid was purified by recrystallization from boiling water, and its composition established by analyses of its silver and copper salts. (See below.)

Properties. — It crystallizes in white glistening flattened needles with but little odor, melts at 114.5°, sublimes above its melting-point in little plates, and burns with the usual luminous green-bordered flame. It is but slightly soluble in cold, freely in boiling water, and in alcohol, ether, benzole, carbonic disulphide, and glacial acetic acid. Ammonic and sodic hydrates dissolve it at once, forming the corresponding salts; it seems to decompose carbonates, but very slowly and imperfectly: potassic dichromate and dilute sulphuric acid convert it with some difficulty into parabrombenzoic acid melting in an impure state near 240°.

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* Zeitschr. Chem. 1866, p. 653.

In 1869, Br. Radziszewski [*] obtained a substance which he called parabromalphatoluylic acid, by the action of bromine in the cold upon alphatoluylic acid; he does not describe it fully, but only says that it crystallizes in prisms melting at 76°, and gives baric and calcic salts crystallizing in warts, and easily soluble in water and alcohol, by oxidizing it with potassic dichromate and dilute sulphuric acid he obtained nothing but parabrombenzoic acid melting at 251°. He also obtained in the same operation another acid containing bromine, which melted at 99°, and was not further examined. The discrepancy between my results and those of Radziszewski, is probably due to the fact that he did not obtain a pure parabromalphatoluylic acid, but that the two acids observed by him were mixtures of para and ortho compounds, with perhaps some of the phenylbromacetic acid, C_6H_5CHBrC OOH, melting-point 82°, discovered by him in conjunction with Glaser,[†] and which he shows in the paper under discussion, is formed from the alphatoluylic acid by the action of bromine at 150°. The presence of a small quantity of orthobromalphatoluylic acid could easily lower the melting-point from 114.°5 to 99°, or even 76°; and, as it would be entirely consumed by oxidizing with potassic dichromate and sulphuric acid, such a mixture would yield only parabrombenzoic acid. On the other hand, my acid being prepared from pure parabrombenzyl-bromide, by processes in which the temperature never rose above 100°, must be perfectly free from isomeres; and this view is confirmed by the fact that its melting-point is higher than that of the acid obtained by Radziszewski.

Ammonic parabromalphatoluate obtained by dissolving the acid in ammonic hydrate, and driving off the excess of ammonia on the water-bath, crystallized in long curving groups of colorless needles very soluble in water.

Argentic parabromalphatoluate ($C_6H_4Br.CH_2COOAg.$) was precipitated by adding the ammonic salt to argentic nitrate, as a white curdy mass similar in appearance to chloride of silver; it was washed with cold water, and dried at 60°.

0.3106 gr. of the salt dissolved in dilute nitric acid, and precipitated with hydrochloric acid, gave 0.1375 gr. AgCl.

	Required for $C_7Br.H_6CO_2$ Ag.	Found.
Silver	33.57	33.33

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[*] Radziszewski, Ber. D. Ch. G., 1869, p. 207.

[†] Zeitschr. Chem., 1868, p. 140.

It is almost insoluble in water, perhaps a little more soluble in hot than in cold, but it could not be obtained crystallized; it is readily soluble in dilute nitric acid; it blackens slightly by exposure to the light, and even at a temperature of 60°.

Cupric parabromalphatoluate, $Cu\,(C_6H_4Br\,CH_2COO)_2$, was precipitated as a flocculent bluish green solid, on mixing cupric sulphate with the ammonic salt.

0.3028 gr. of the salt gave 0.05028 CuO.

	Required for $Cu(C_8H_6Br.O_2)_2$.	Found.
Copper	12.90	13.24

It is insoluble in water, but soluble in dilute hydrochloric acid.

The *baric salt*, obtained by neutralizing a solution of the acid with baryta water and evaporating, formed white indistinctly crystalline crusts easily soluble in water.

The *calcic salt* obtained in a similar way, and also, although very slowly from calcic carbonate and a solution of the acid, appeared in the form of white warts; which, under the microscope, were seen to be globular groups of sharp needles looking somewhat like a chestnut-bur; it was easily soluble in water.

The behavior of a solution of ammonic parabromalphatoluate with solutions of the following salts was also observed: —

Mercurous salts, a heavy flocculent white precipitate.

Mercuric salts, a slight white precipitate.

Plumbic salts, a heavy white precipitate, somewhat soluble in boiling water, and separating from this solution in crystalline flocks.

Ferric salts, a pale yellow amorphous precipitate, while Chromic, Aluminic, Manganous, Cobaltous, Nickelous, Zincic, and Magnesic salts produced no precipitate.

Triparabrombenzylamine, $(C_6H_4Br.CH_2)_3N$, was formed even in the cold, when alcoholic ammonia was added to the parabrombenzylbromide; the white crystals which separated in large quantity were washed with water, and then recrystallized repeatedly from alcohol; in this way the triparabrombenzylamine was easily separated from its bromhydrate, which is very slightly soluble even in hot alcohol, and two sorts of crystals of the former substance were obtained, one in irregular somewhat bent thick needles, the other in fan-shaped groups of fine needles, both had the same melting-point, seemed to be about equally soluble in alcohol, and mutually convertible under conditions which could not be determined; it was therefore assumed that they were identical, and this assumption seems to be confirmed by the following analyses: —

I. 0.5397 gr. of the thicker needles gave 12 cc. nitrogen, at 757.4 mm., and 20° t.

II. 0.2664 gr. of the fan-shaped crystals gave 5.2 cc. nitrogen, at 763.1 mm. and 17.°5. t.

	Required for $(C_7H_6Br.)_3N$.	Found.	
		I.	II.
Nitrogen	2.67	2.53	2.26

Owing to the small amount of the fan-shaped crystals which could be isolated, I have not been able to establish its composition more securely by a second analysis.

Properties. — It crystallizes either in thick irregular white prisms or fan-shaped groups of white needles, is odorless, melts at 78°–79°, burns with the green-bordered luminous flame belonging to all these compounds, and is insoluble in water, soluble in cold, more so in hot alcohol, freely soluble in ether, benzole, and carbonic disulphide. All attempts to obtain a salt with hydrochloric acid alone, or in connection with platinic chloride were unsuccessful.

Triparabrombenzylamine bromhydrate, $(C_6H_4Br.CH_2)_3NH\,Br$, was formed at the same time as the free base, and separated from it by boiling out the product of the reaction, with alcohol; the viscous residue left after the removal of the triparabrombenzylamine by this means was dissolved in ether, from which it crystallized on evaporation.

0.4269 gr. of the substance gave 8 cc. nitrogen, at 767.7 mm. and 17° t.

0.4713 gr. of substance gave 0.5818 gr. AgBr.

	Required for $(C_7H_6Br.)_3NH\,Br$.	Found.
Nitrogen	2.29	2.19
Bromine	52.54	52.54

Properties. — White odorless plates with a pearly lustre, melting in the neighborhood of 270°, is insoluble in hot or cold water, almost insoluble in alcohol even when boiling, soluble although not very easily in ether, gives no double salt with platinic chloride.

The formation of triparabrombenzylamine as the principal product of the reaction is not to be wondered at, as benzylbromide gives a similar result when treated with alcoholic ammonia (Kekule*). It is not impossible, however, that some di- or even mono-parabrombenzylamine bromhydrate was formed, as this would undoubtedly have been dissolved in washing the product of the reaction with water, and this wash-water was unfortunately lost before it was investigated.

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* Kekule Ann. Chem. Pharm., 137, p. 188.

Parabrombenzylsulphocyanate ($C_6H_4Br.CH_2SCN$) was obtained by boiling the bromide with alcoholic potassic sulphocyanate, and purifying by crystallizing from alcohol at low temperatures. I have but one imperfect sulphur determination of this substance, but have not thought it of sufficient importance to go through the purification of a fresh quantity, which is rendered difficult by its low melting-point, in order to confirm this result.

0.2455 gr. of substance gave .2339 gr. of $Ba.SO_4$.

	Required for $C_7H_6Br.SCN$.	Found.
Sulphur	14.03	13.08

Properties. — It forms white ribbons often 5 cm. long, made up of needles united together laterally, having a strong odor similar to that of benzylsulphocyanate, melting at 25°, and soluble in alcohol. The surprisingly low melting-point rendered the management of the substance very difficult, and preserving the crystals impossible; it also — as the benzylsulphocyanate melts at 36°–38°, according to Henry;* at 41°, according to Barbaglia† — throws doubt on the analysis given above, and therefore on the correctness of the formula.

The investigation of the parabrombenzyl compounds will be continued in this laboratory; the next portion of the subject to be studied being the action of heat, superheated steam, and sodium on these bodies.

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* Henry, Ber. D. Ch. G., 1869, p. 637.

‡ Barbaglia, Ber. D. Ch. G., 1872, p. 687.